

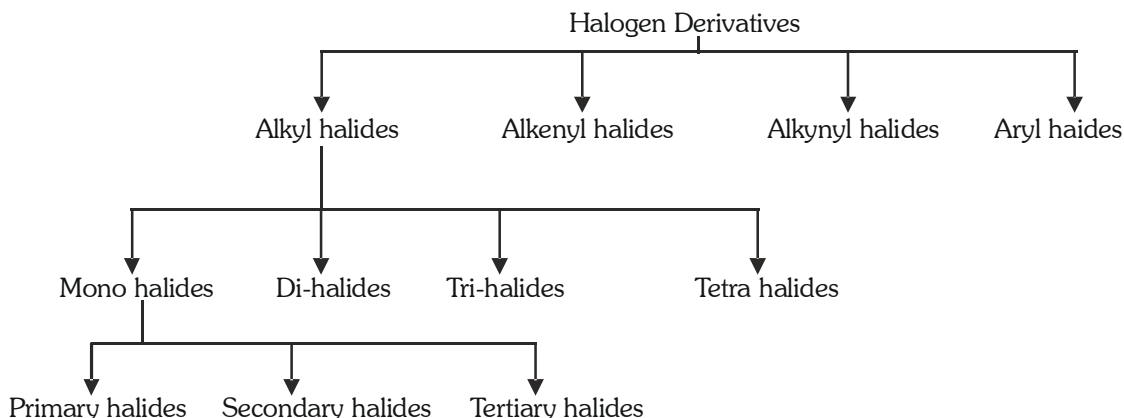
HALOGEN DERIVATIVES

1.0 HALOGEN DERIVATIVES

Compounds derived from hydrocarbons by replacement of one or more H-atoms by corresponding no. of halogen atoms are known as halogen derivatives.

2.0 CLASSIFICATION

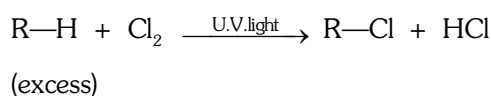
On the basis of nature of hydrocarbon from which they are obtained, halogen derivatives can be classified as :



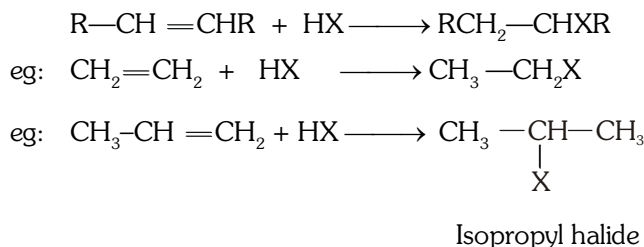
3.0 MONOHALIDES :

3.1 Genreal Methods of Preparation of Monohalides

(1) By direct halogenation of alkanes :

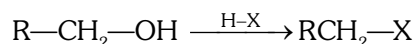


(2) By the addition of H—X on alkenes :

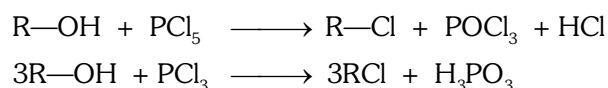


(3) By Alcohols :

(a) By the action of hydrogen halides :

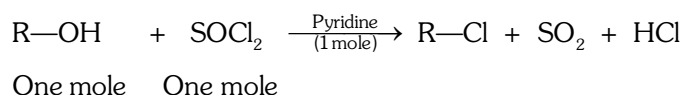


(b) By the action of phosphorous halides :



PBr₃ and PI₃ are less stable, thus for bromides (P + Br₂) and for iodides (P + I₂) mixture is used.

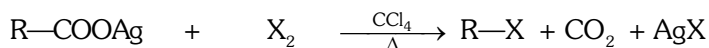
(c) By reaction with thionyl chloride (Darzen's procedure) :



Because of less stability of SOBr₂ and SOI₂, R—Br and RI can not be obtained by this method.



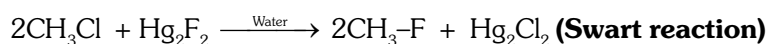
(4) Borodine – Hunsdicker's reaction :



Silver salt of (Cl₂ or Br₂)

a fatty acid

(5) By halide exchange :



Note : Finkelstein reaction can only be used to prepare R-I and swart's reaction can only be used to prepare R-F

3.2 Physical Properties

(a) The lower members CH₃F, CH₃Cl, CH₃Br, C₂H₅Cl and C₂H₅F are gases at room temp.

(b) Higher B.P. than parent alkanes.

Decreasing order of B.P. is : **R-I > R-Br > R-Cl > R-F**

among isomeric R-X, decreasing order of B.P. is : **Primary > Secondary > tertiary**

(c) R-F and R-Cl → lighter than water

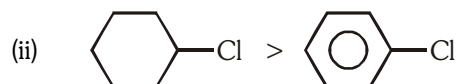
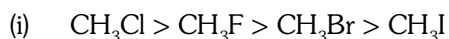
R-Br and R-I → heavier than water

Decreasing order of density is : **R-I > R-Br > R-Cl > R-F**

(d) R-X are polar co-valent compounds but insoluble in water because they can not form H-bonds. They dissolve in organic solvents.

(e) R-X (except R-F) burns with a green flame when interacted with Cu wire.(Beliestein test)

(f) Dipole moment order-



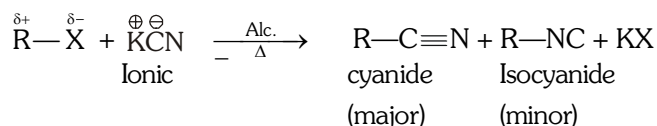
3.3 Chemical Properties

3.3.1 Nucleophilic substitution reaction (S_N) :

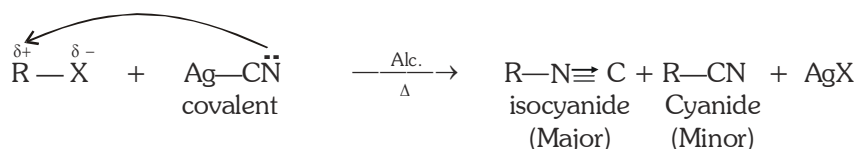
	Replacement of	Product
(a)	$\xrightarrow[\text{X by } -OH]{HOH(Boil)}$	R-OH (alcohol) + HX
(b)	$\xrightarrow[\text{X by } -OH]{KOH aq.}$	R-OH (alcohol) + KX
(c)	$\xrightarrow[\text{X by } -OH]{moist Ag_2O}$	R-OH (alcohol) + AgX
(d)	$\xrightarrow[\text{X by } -SH]{KSH alc.}$ (Mercapto Gp.)	R-SH + KX Alkane thiol (Mercaptane)
(e)	$\xrightarrow[\text{X by } SR]{NaSR'}$	RSR' + NaX Thioether
(f)	$\xrightarrow[\text{X by } (R'COO)]{R' COOAg, \Delta}$	R' COOR + AgX (Alkyl alkanoate) ester



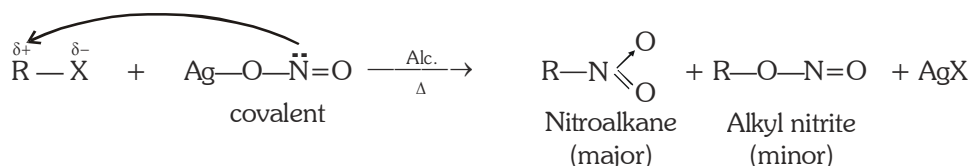
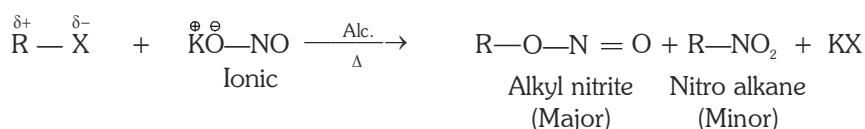
(g) Reaction with KCN and AgCN :



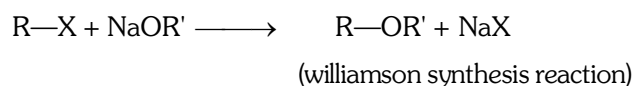
● $\text{:}\ddot{\text{C}}\text{N}^\ominus$ ion is an ambident nucleophile.



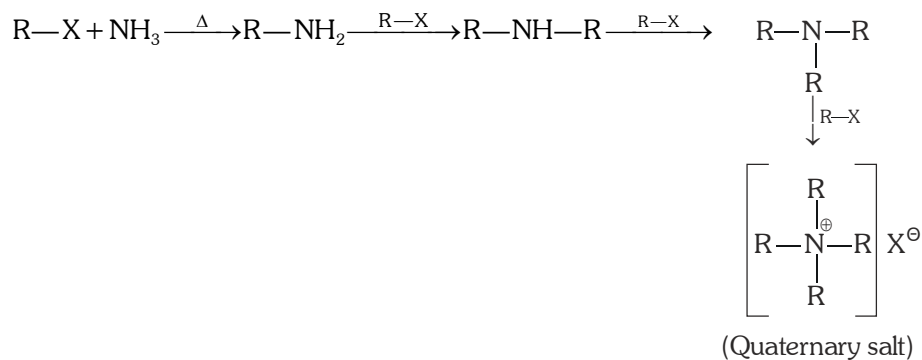
(h) Reaction with KNO_2 and AgNO_2 :



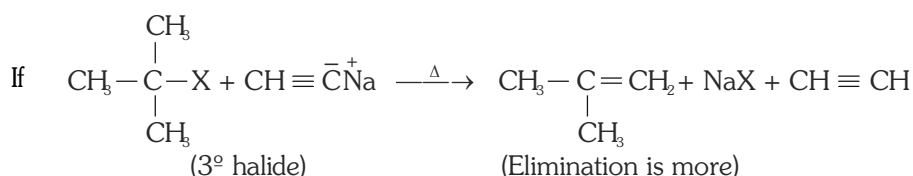
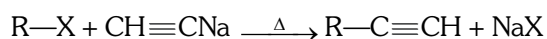
(i) Reaction with NaOR' (Sodium alkoxide) :



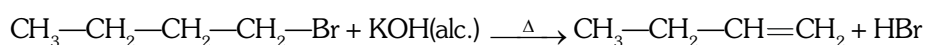
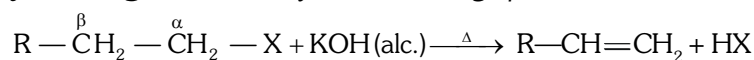
(j) Reaction with NH_3 :



(k) Reaction with $\text{CH}\equiv\text{CNa}$:



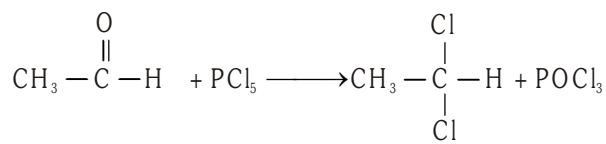
3.3.2 Dehydrohalogenation : Alkyl halides undergo β - elimination on treatment with KOH (alc.) or NaNH_2 .



4.1 General Methods of Preparation

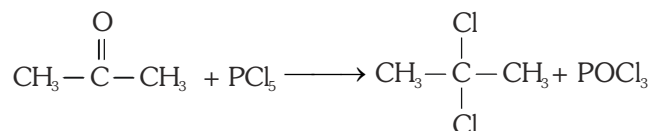
(a) Gem dihalides :

- (i) By the reaction of PCl_5 on carbonyl compound.



Acetaldehyde

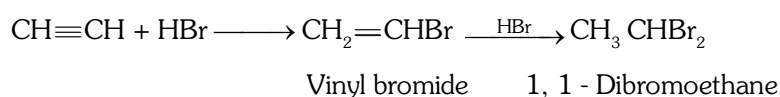
Ethylidene chloride



Acetone

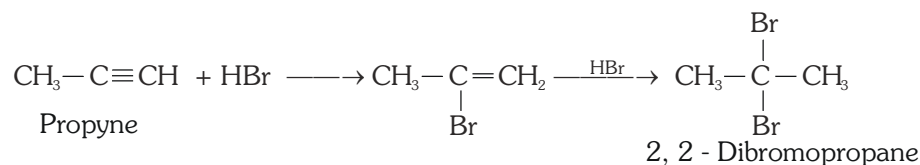
2, 2 - Dichloropropane

- (ii) By addition of halogen acids on alkynes :



Vinyl bromide

1, 1 - Dibromoethane

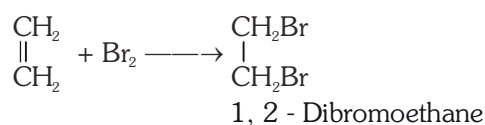


Propyne

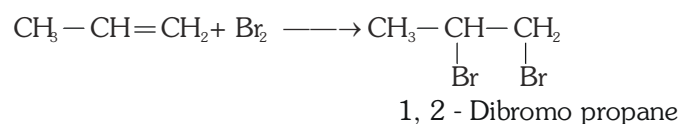
2, 2 - Dibromopropane

(b) Vic-dihalides :

- (i) By the addition of halogens to alkenes :

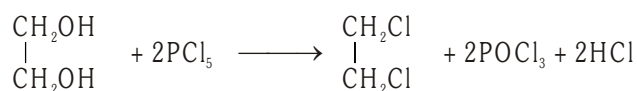


1, 2 - Dibromoethane



1, 2 - Dibromo propane

- (ii) By the action of PCl_5 on glycols :



4.2 Physical Properties

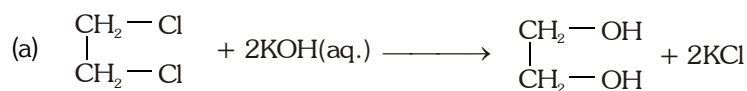
- (i) Lower members are colourless, oily liquids with sweet smell. Higher members are solid.
- (ii) These are heavier than water.

4.3 Chemical Properties

- (i) Action of KOH(alc.) :** (Dehydrohalogenation)



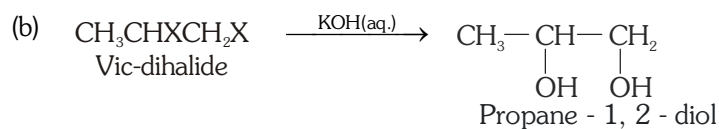
(ii) Action of KOH(aq.) : (Hydrolysis) It is a distinction test for gem - and vic - dihalides.



Glycol

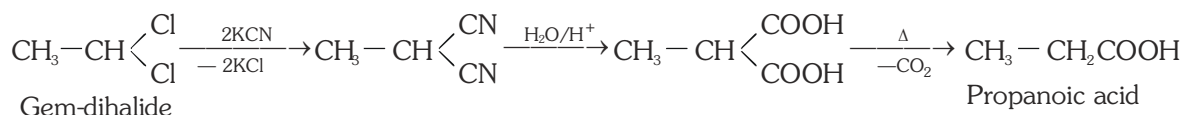
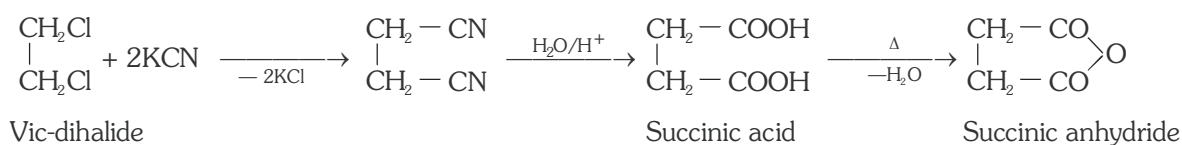
Vic-dihalide.

1, 2 - Ethanediol



Gem-dihalides

(iii) Reaction with KCN :

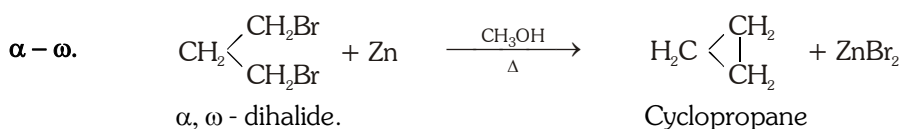
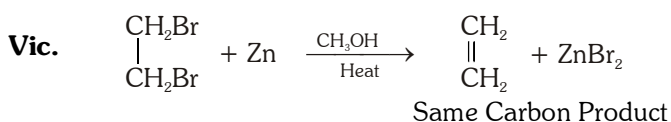


(i) - CN group on acid hydrolysis gives - COOH

(ii) Two - COOH group on one C - atom always lose CO₂ to form monocarboxylic acid on heating.

(iii) Two - COOH group on vic. C - atom lose H₂O to form cyclic anhydride on heating.

(iv) Dehalogenation :



BEGINNER'S BOX-1

1. Which of the following is not organometallic compound

- (1) RMgX (2) R₂Zn (3) RNa (4) R₂Hg

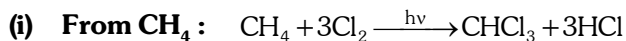
2. Which is Finkelstein reaction ?

- (1) R-X + NaI $\xrightarrow{\text{acetone}}$ (2) R-X + AgF \longrightarrow
 (3) R-X + NaF \longrightarrow (4) R-F + AgCl \longrightarrow

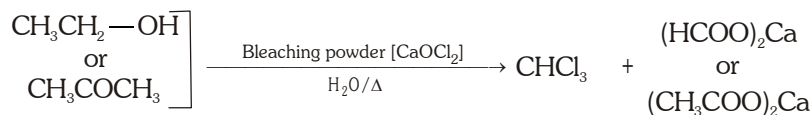


5.0 TRI HALIDES (Haloform CHX_3)

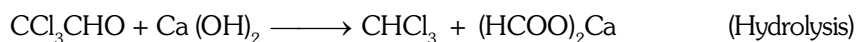
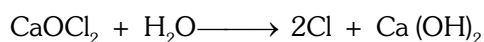
5.1 General Method of Preparation



(ii) **By Haloform reaction (lab method) :**



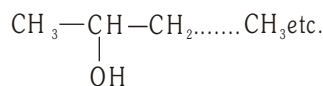
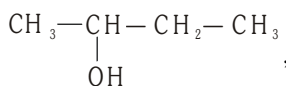
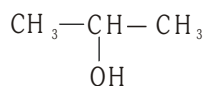
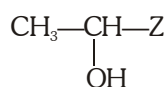
Mechanism :



If CH_3COCH_3 is used then CHCl_3 is formed into 2 steps (Chlorination and Hydrolysis)

(+) ve haloform reaction : Reaction which gives haloform with alkali and X_2 is called as (+) ve haloform reaction.

Ex. Alcohols :



Aldehydes : Only acetaldehyde $\text{CH}_3-\text{C}-\text{H}$
 \parallel
 O

Ketones : $\text{CH}_3-\text{C}-\text{Z}$
 \parallel
 O

Ex . $\text{CH}_3-\text{C}-\text{CH}_3$, $\text{CH}_3-\text{C}-\text{CH}_2-\text{CH}_3$, $\text{CH}_3-\text{C}-\text{CH}_2\cdots\cdots\text{CH}_3$ etc. (All methyl ketones)
 \parallel \parallel \parallel
 O O O

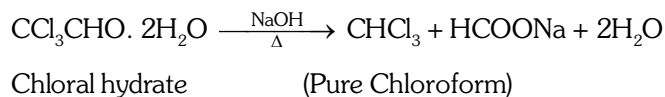
$\text{CH}_3-\text{C}-\text{COOH}$, $\text{CH}_3-\text{C}-\text{CHO}$ Also show haloform reaction.
 \parallel \parallel
 O O

(-) ve haloform reaction : Reaction in which haloforms are not formed with X_2 and alkali.

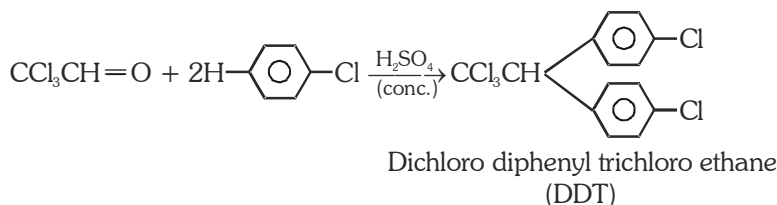
Ex. $\text{CH}_3-\text{C}-\ddot{\text{Cl}}$, $\text{CH}_3-\text{C}-\ddot{\text{O}}\text{H}$, $\text{CH}_3-\text{C}-\ddot{\text{N}}\text{H}_2$, $\text{CH}_3-\text{C}-\ddot{\text{O}}-\text{CH}_3$. do not show haloform reaction.
 \parallel \parallel \parallel \parallel
 O O O O



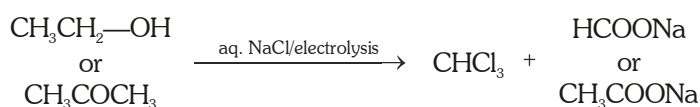
(iii) Preparation of pure CHCl_3 :



Chloral can also be used in preparation of D.D.T.



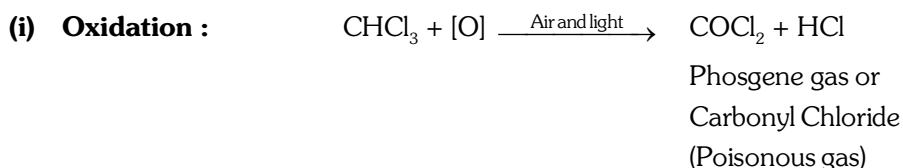
(iv) Industrial preparation :



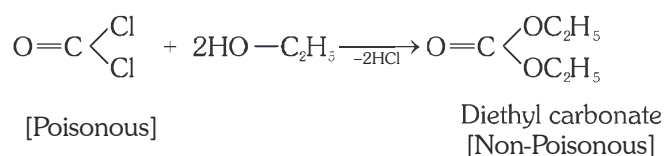
5.2 Physical Properties

CHCl_3 is colourless and sweet smelling liquid. It's B.P. is 61°C and it is insoluble in H_2O and have density more than H_2O . Chloroform is used as Anaesthetic.

5.3 Chemical Properties



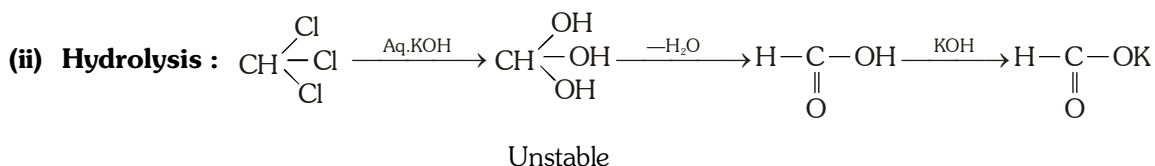
CHCl_3 is stored in dark coloured bottles which are filled upto the brim to prevent oxidation of CHCl_3 into COCl_2 and 1% ethanol is also added to chloroform



GOLDEN KEY POINTS

Test of CHCl_3

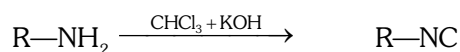
Reagent	Pure CHCl_3	Impure CHCl_3 ($\text{COCl}_2 + \text{HCl}$)
• Blue litmus	No Change	turns into red
• AgNO_3	No reaction	White ppt of AgCl
• Conc. H_2SO_4	No reaction	Yellow solution



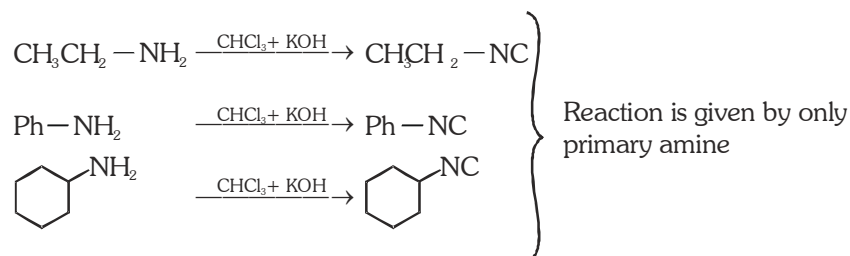
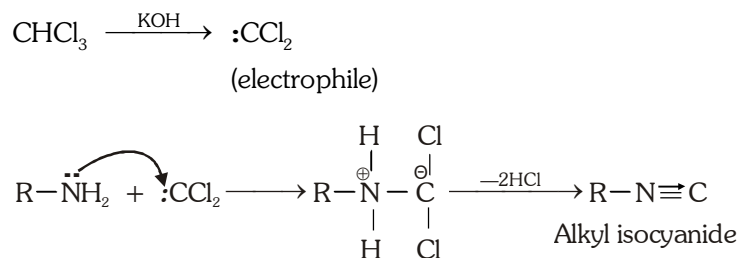
(iii) Carbyl amine reaction or isocyanide test : (Hoffman's carbylamine reaction)

Primary-Amines (Aliphatic or Aromatic) $\xrightarrow{\text{CHCl}_3 + \text{KOH}}$ Isocyanides

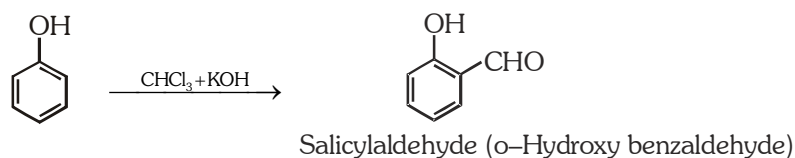
Isocyanides have unpleasant or offensive smell (Isocyanide test).



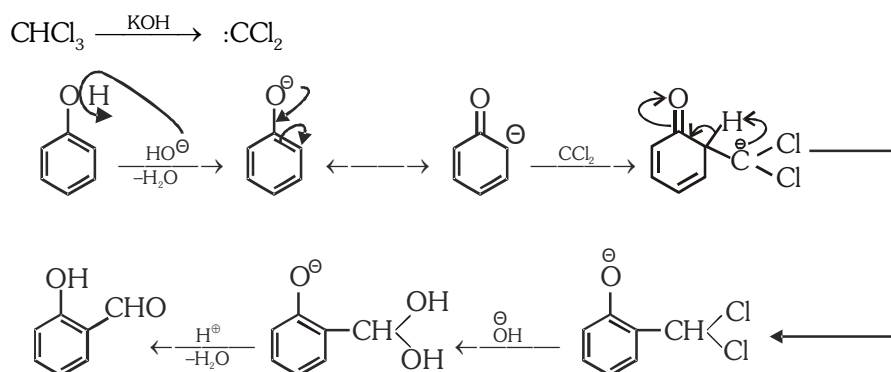
Mechanism :



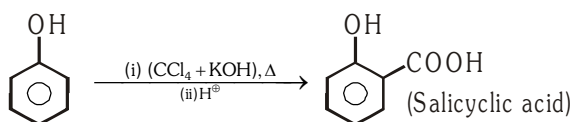
(iv) Reimer Tieman's reaction :



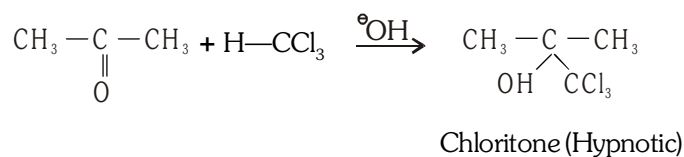
Mechanism : :CCl_2 is neutral attacking electrophile (formed by α, α -elimination reaction)



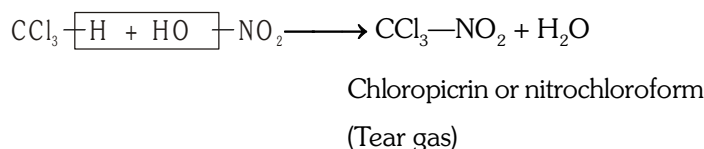
Note : If CCl_4 is used in place of chloroform, salicylic acid is formed as product.



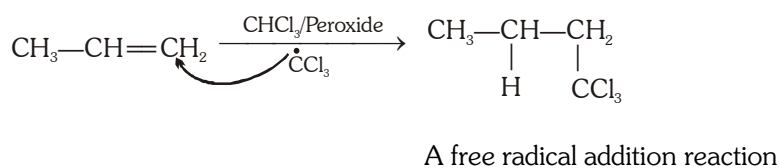
(v) Reaction with CH_3COCH_3 :



(vi) Reaction with HNO_3 :



(vii) Reaction with $\text{CH}_3\text{CH}=\text{CH}_2$:

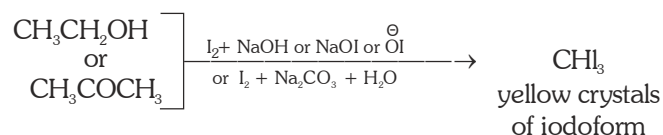


(viii) Reaction with Ag : $\text{CHCl}_3 \xrightarrow{\text{Ag}} \text{CH}\equiv\text{CH}$

(ix) FCR : $3\text{Ph}-\text{H} + \text{CHCl}_3 \xrightarrow{\text{AlCl}_3} \text{Ph}_3\text{CH}$
Triphenyl methane

GOLDEN KEY POINTS

Iodoform Test



- CHI_3 give yellow ppt. of AgI with AgNO_3 but CHCl_3 does not give AgCl ppt.

Reason : CHI_3 is thermally less stable than CHCl_3 .

Iodoform test can be used to distinguish the following pairs of compounds.

- $\text{CH}_3\text{CH}_2\text{OH}$ and CH_3OH
- CH_3CHO and $\text{CH}_3\text{CH}_2\text{CHO}$
- 2-Pentanol and 3-Pentanol
- Acetophenone and benzophenone
- 2-Propanol and 1-Propanol

Freons

The chlorofluoro derivatives of methane and ethane are called freons.

CF_2Cl_2 – (dichloro difluoro methane)

$\text{C}_2\text{F}_2\text{Cl}_4$ – (Tetrachloro difluoroethane)

Most useful is CF_2Cl_2 (Freon- 12)



Nomenclature of freons :

Freon – cba

$$c = n_{C-1}$$

$$b = n_{H+1}$$

$$a = n_F$$

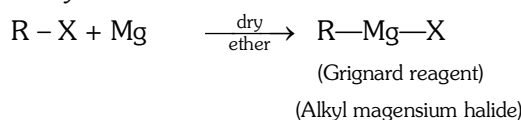


- Excess use of Freons is harmful for Ozone layer (depletion of Ozone layer).

6.0 Grignard Reagent

6.1 General Method of Preparation


Grignard reagents are prepared in the laboratory by the action of alkyl halides on magnesium metal in the presence of dry ether.



The ease of formation of Grignard reagent is in the order $\text{RI} > \text{RBr} > \text{RCl}$

Ether is used to dissolve the Grignard reagent by coordination.

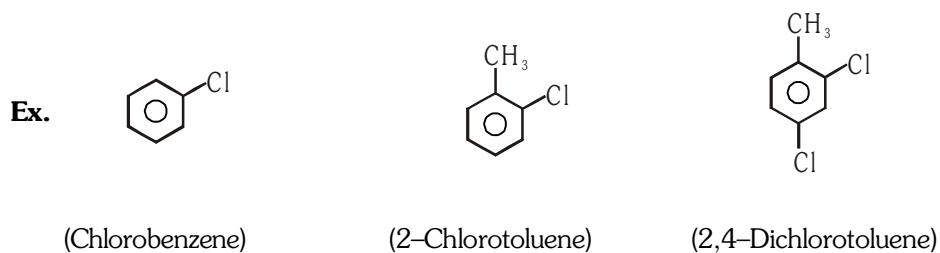
6.2 Chemical Reactions

R-Mg-X	(i) O_2 (ii) H_3O^+	R-OH	1° Alcohol
	$\text{H}_2\text{C=O}/\text{H}_3\text{O}^+$	$\text{RCH}_2\text{-OH}$	1° Alcohol
	 $\text{CH}_2\text{-CH}_2/\text{H}_3\text{O}^+$	$\text{R-CH}_2\text{-CH}_2\text{-OH}$	1° Alcohol
	$\text{RCHO}/\text{H}_3\text{O}^+$	R_2CHOH	2° Alcohol
	$\text{HCOOEt}/\text{H}_3\text{O}^+$	R_2CHOH	2° Alcohol
	$\text{RCOR}/\text{H}_2\text{O}$	$\text{R}_3\text{C-OH}$	3° Alcohol
	$\text{RCOOEt}/\text{H}_2\text{O}$ (2 : 1)	$\text{R}_3\text{C-OH}$	3° Alcohol
	HCOOEt (1 : 1)	RCHO	aldehyde
	$\text{RCN}/\text{H}_2\text{O}$	RCOR	Ketone
	RCOOEt (1 : 1)	RCOR	Ketone
	$\text{CO}_2/\text{H}_2\text{O}$	RCOOH	Acids
	HOH or ROH or NH_3 or Ph-OH or R-NH_2 or RNH-R or $\text{CH}\equiv\text{CH}$ or Ph-NH_2	R-H	Alkane
	R-X	R-R	Alkane
	R_3N	No reaction	
	$\text{ClCH}_2\text{-CH=CH}_2$	$\text{R-CH}_2\text{-CH=CH}_2$	Alkene
	Cl-NH_2	R-NH_2	1° Amine
	Cl-CN	R-CN	Cyanides
	ClCOOEt	RCOOEt	Ester

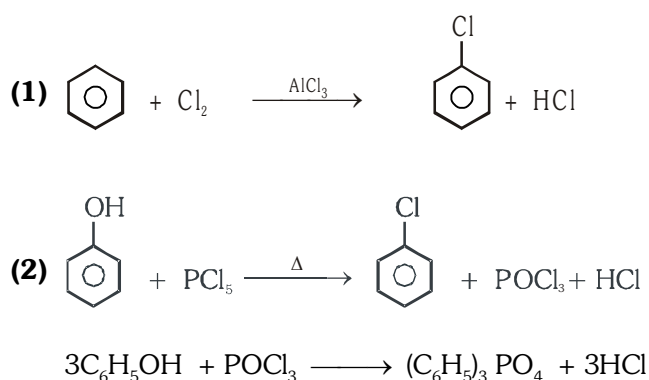


7.0 Haloarene

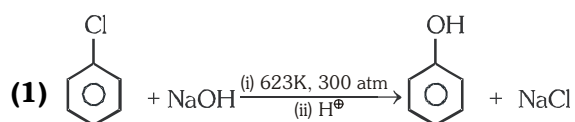
If halogen atom is directly attached to the benzene ring, then compound is called as Haloarene.



7.1 General Methods of Preparation

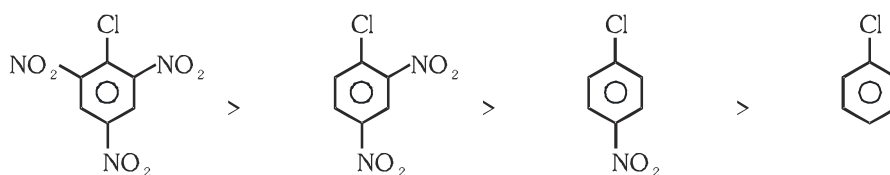


7.2 Chemical Properties

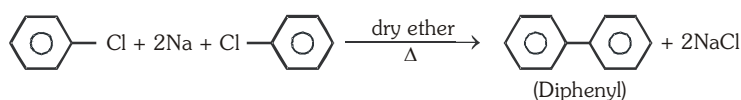


Presence of electron withdrawing group on ring makes the nucleophilic substitution easier.

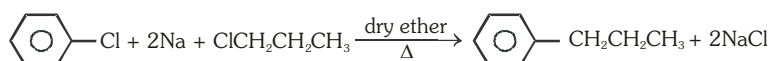
Reactivity Order : (Towards nucleophilic substitution)



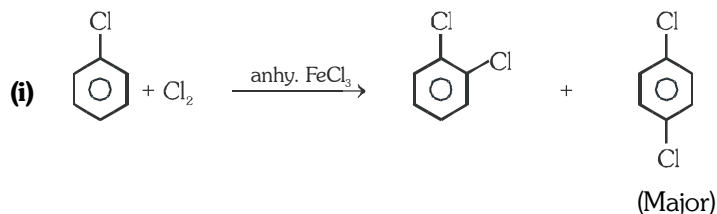
(2) Fittig reaction :



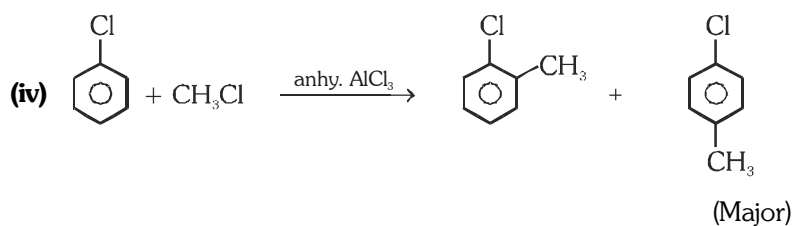
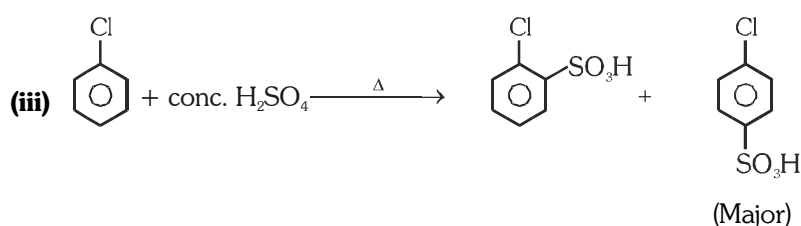
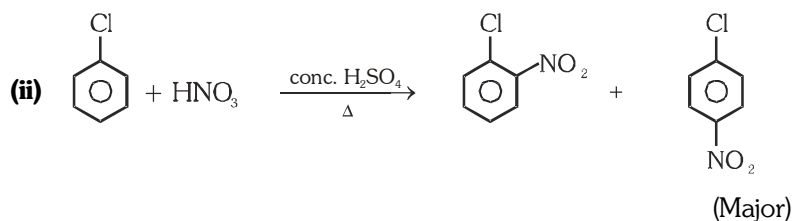
(3) Wurtz fittig reaction :



(4) Electrophilic Substitution Reaction :



Note : Cl is o- and p- directing group.



BEGINNER'S BOX-2

- Which can give haloform with X_2/OH^- ?
 (1) CH_3OH (2) $CH_3-CH_2-CH=O$
 (3) CH_3CHO (4) $CH_3CH_2CH_2OH$
- Which of the following compounds cannot be identified by carbylamine test ?
 (1) $C_6H_5-NH-C_6H_5$ (2) $CH_3CH_2NH_2$
 (3) $CHCl_3$ (4) $C_6H_5-NH_2$
- For preparation of Grignard reagent from haloalkanes which metal is used :-
 (1) Na (2) Mg
 (3) Ca (4) Ag

ANSWER KEY

BEGINNER'S BOX-1	Que.	1	2								
	Ans.	3	1								

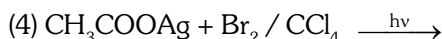
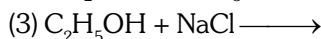
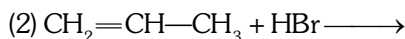
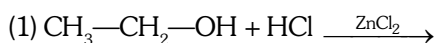
BEGINNER'S BOX-2	Que.	1	2	3							
	Ans.	3	1	2							



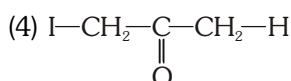
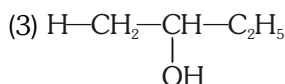
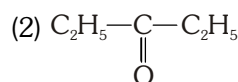
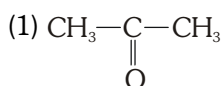
EXERCISE-I (Conceptual Questions)

GENERAL METHOD OF PREPARATION

1. Alkyl halides can be obtained by all methods excepts



2. Which of the following will not give iodoform test



3. Which of the following product is obtained when bleaching powder is distilled with acetone



4. Which will give yellow ppt. with iodine and alkali

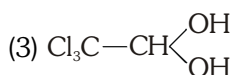
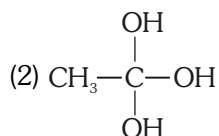


PHYSICAL PROPERTIES

5. Which of the following has the highest boiling point



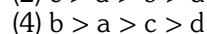
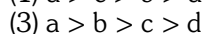
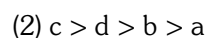
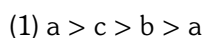
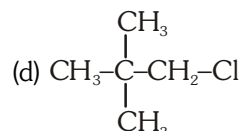
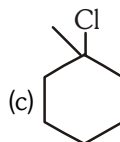
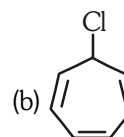
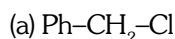
6. A compound containing two —OH groups attached with one carbon atoms is unstable but which one of the following is stable



(4) All

CHEMICAL PROPERTIES

7. Arrange the following compounds in decreasing order of reactivity in $\text{S}_\text{N}1$ reaction :-



8. $\xrightarrow{\text{CHCl}_3 + \text{KOH}}$ Product.

about above reaction the incorrect statement is

(1) The name of reaction is Reimer-Tsima's reaction

(2) The intermediate in the reaction is dichloro carbene

(3) The final product is salicylaldehyde

(4) The final product is benzyl chloride

9. The purity of CHCl_3 can be checked by

(1) treating CHCl_3 by NaOH

(2) treating CHCl_3 by HCl

(3) treating CHCl_3 with aq. AgNO_3

(4) treating CHCl_3 by $\text{C}_2\text{H}_5\text{—OH}$

10. Pure CHCl_3 and pure CHI_3 can be distinguished by

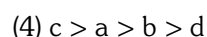
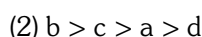
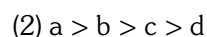
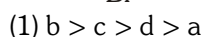
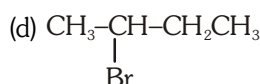
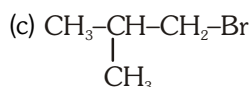
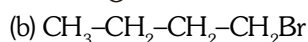
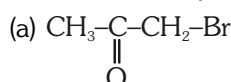
(1) treating with litmus paper

(2) treating with aq. KOH

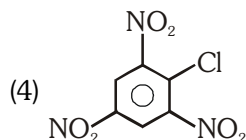
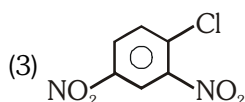
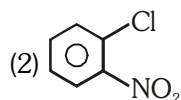
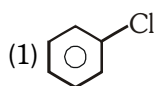
(3) treating with HCl

(4) treating with aq. AgNO_3

11. Arrange the following compound in decreasing order of reactivity in $\text{S}_\text{N}2$ reaction.



12. Which of the following undergoes hydrolysis most easily



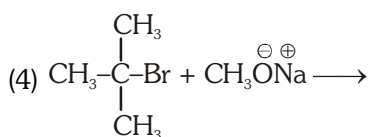
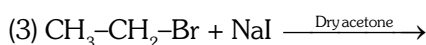
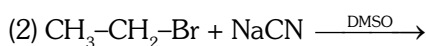
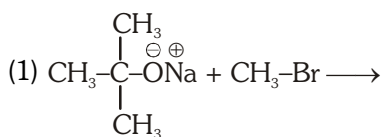
13. Which of the following is used as insecticide

- (1) D.D.T. (2) Chloritone
(3) CHCl_3 (4) All of them

14. Which of the following when heated with KOH and primary amine gives carbylamine test

- (1) CHCl_3 (2) CH_2Cl_2
(3) CH_3OH (4) CCl_4

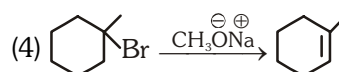
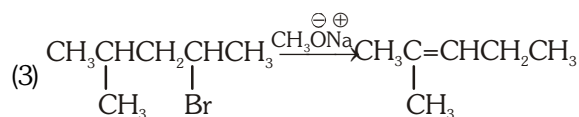
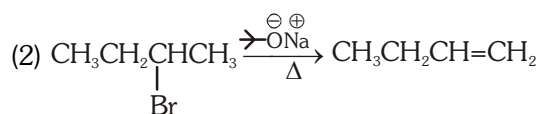
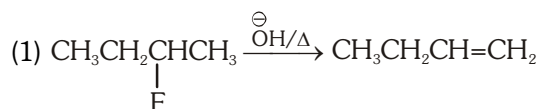
15. Which reaction gives elimination as a major product



16. Iodoform gives a precipitate with AgNO_3 on heating but chloroform does not because

- (1) Iodoform is ionic
(2) Chloroform is covalent
(3) C-I bond in iodoform is weak and C-Cl bond in chloroform is strong
(4) None of the above

17. Which reaction product is wrong (major) product.



18. When alkyl magnesium halide reacts with R-NH_2 , the product is

- (1) R-R (2) R-H
(3) R_2NH (4) R-X

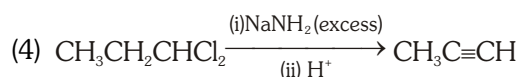
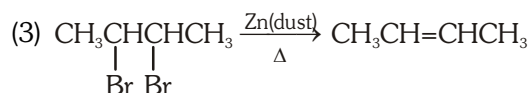
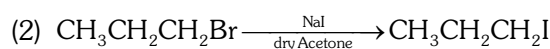
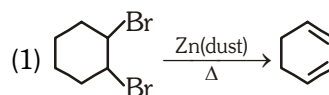
19. Chloroform on reaction with acetone gives:-

- (1) Acetylene (2) Chloroform
(3) Nitrochloroform (4) Chloroacetone

20. Chloroform reacts with aniline and aqueous KOH gives :-

- (1) $\text{Ph-N} \equiv \text{C}$ (Phenyl isocyanide)
(2) Benzene
(3) Phenyl cyanide
(4) None of these

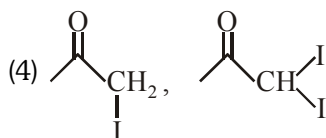
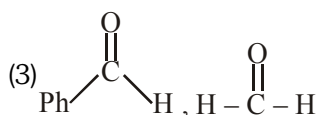
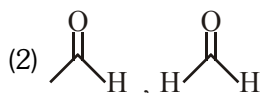
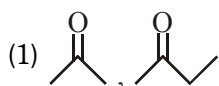
21. Which reaction product is wrong (major) product



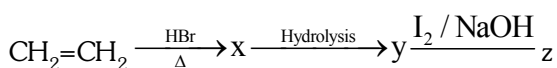
22. Which of the following undergoes nucleophilic substitution by $\text{S}_{\text{N}}1$ mechanism at fastest rate :



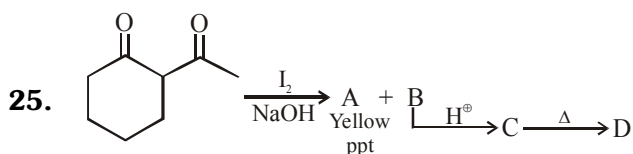
23. Which of the following pair is differentiated by iodoform test?



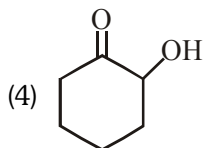
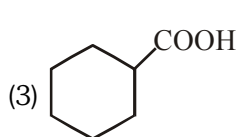
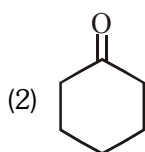
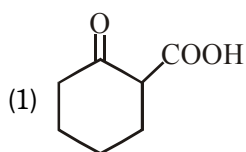
24. Identify z in the following series



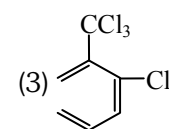
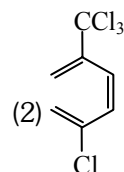
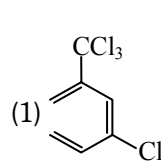
- (1) $\text{C}_2\text{H}_5\text{I}$ (2) $\text{C}_2\text{H}_5\text{OH}$
(3) CHI_3 (4) CH_3CHO



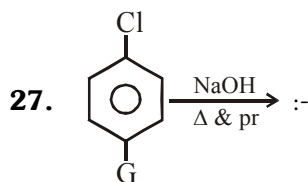
Identify D :-



In the above reaction X is



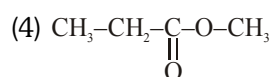
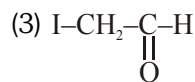
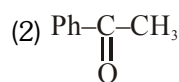
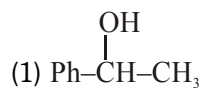
(4) None of these



Rate of reaction is maximum if G is :-

- (1) $-\text{OCH}_3$ (2) $-\text{CH}_3$
(3) $-\text{NO}_2$ (4) $-\text{H}$

28. Which does not gives iodoform test :-



EXERCISE-I (Conceptual Questions)

ANSWER KEY

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	3	2	2	1	1	3	4	4	3	4	2	4	1	1	4
Que.	16	17	18	19	20	21	22	23	24	25	26	27	28		
Ans.	3	3	2	2	1	1	3	2	3	2	1	3	4		



EXERCISE-II (Assertion & Reason)**Directions for Assertion & Reason questions**

These questions consist of two statements each, printed as Assertion and Reason. While answering these Questions you are required to choose any one of the following four responses.

- (A) If both Assertion & Reason are True & the Reason is a correct explanation of the Assertion.
 (B) If both Assertion & Reason are True but Reason is not a correct explanation of the Assertion.
 (C) If Assertion is True but the Reason is False.
 (D) If both Assertion & Reason are false.
- Assertion :-** Alkyl halides are not soluble in water.
Reason :- Alkyl halide does not form H-bonds with water molecule although alkyl halide is polar in nature.
 (1) A (2) B (3) C (4) D
 - Assertion :-** CHCl_3 is more acidic than CHF_3 .
Reason :- Electronegativity of Fluorine is more than chlorine.
 (1) A (2) B (3) C (4) D
 - Assertion :-** Isobutanol does **not** give iodoform test.
Reason :- It does not have α -hydrogen.
 (1) A (2) B (3) C (4) D
 - Assertion :-** Styrene on reaction with HBr gives 1-bromo-1-phenylethane.
Reason :- Benzyl radical is more stable than alkyl radical.
 (1) A (2) B (3) C (4) D
 - Assertion :-** Rate of alkaline hydrolysis of methyl chloride to methanol is higher in DMF than in water.
Reason :- Hydrolysis of methyl chloride follows second order kinetics.
 (1) A (2) B (3) C (4) D
 - Assertion :-** 2-Bromo butane on reaction with alcoholic KOH mainly gives 2-butene.
Reason :- The hydrogen on C_3 carbon is more acidic than hydrogen on C_1 carbon.
 (1) A (2) B (3) C (4) D
 - Assertion :-** Chlorobenzene is less reactive than benzene for electrophilic substitution reaction.
Reason :- Resonance effect in chlorobenzene destabilized carbocation intermediate.
 (1) A (2) B (3) C (4) D

EXERCISE-II (Assertion & Reason)**ANSWER KEY**

Que.	1	2	3	4	5	6	7	
Ans.	1	2	3	2	1	3	3	

